Anal. Calcd. for $C_{12}H_{12}O_4N_2$: N, 11.30. Found: N, 11.21.

5-(Phenyl-β-hydroxyethyl)-2-thiobarbituric Acid.—This compound was prepared by condensation of ethyl phenylvinyloxyethylmalonate with thiourea. The procedure was the same as that given directly above, m. p. 167°. The yield was 15%.

Anal. Calcd. for $C_{12}H_{12}O_3N_2S$: N, 10.6. Found: N, 10.9.

Phenylvinyloxyethylacetonitrile $C_6H_5CH(CH_2CH_2OCH{=}CH_2)CN$.—This nitrile was prepared by reaction of phenylacetonitrile and β-chloro-ethylvinyl ether, according to the general method devised by Bodroux and Taboury.[14] The yield was 50%. The pure compound boils at 147° (8 mm.); $d_4^{20} = 1.029$.

Anal. Calcd. for $C_{12}H_{13}ON$: N, 7.48. Found: N, 7.33.

Summary

1. A convenient method for the preparation of ethyl phenylmalonate has been described.

2. A new barbituric acid closely related to Luminal, 5-phenyl-β-hydroxyethyl-2,4,6-trioxypyrimidine, has been synthesized.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE REACTION BETWEEN THE BINARY SYSTEM, MAGNESIUM + MAGNESIUM IODIDE, AND AROMATIC ACIDS AND ACID DERIVATIVES

BY M. GOMBERG AND W. E. BACHMANN

RECEIVED JULY 9, 1928 PUBLISHED OCTOBER 6, 1928

The interaction of magnesium + magnesium iodide and aromatic ketones results in addition of MgI to the C=O group.[1] A similar reaction occurs with 1,2-diketones,[2] with thio-ketones[3] and apparently with quinones.[4] The MgI, the probable formation of which has been postulated, may thus be regarded as functioning like a monovalent element, as sodium. This comparison holds in reactions that are to be discussed in this communication on acids and in communications to follow, on various classes of compounds containing double and triple bonds.

Reaction of Acids with Magnesium + Magnesium Iodide.—This reaction takes place in two steps: (*a*) displacement of the acid hydrogen by MgI and (*b*) reduction of the resulting salt.

The displacement of hydrogen is best explained by the fact that there is an equilibrium reaction between MgI_2 and the organic acid. Only a small amount of HI results by virtue of this reaction; nevertheless, in the

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[14] Bodroux and Taboury, *Bull. soc. chim.*, [7] **4**, 666 (1910).

[1] Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927).

[2] Gomberg and Bachmann, *ibid.*, **49**, 2584 (1927).

[3] Schönberg and Schütz, *Ber.*, **60**, 2351 (1927).

[4] Fieser, THIS JOURNAL, **50**, 464 (1928).

presence of metallic magnesium, which reacts with the HI, the reaction proceeds quantitatively according to the following formulation

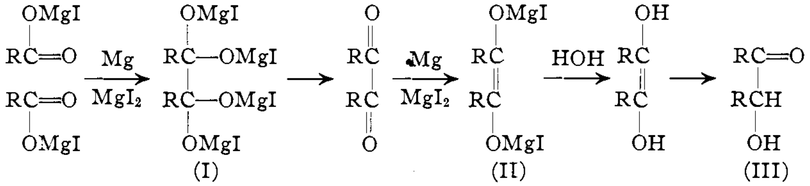
$$2\mathrm{RCOOH} + \mathrm{Mg} + \mathrm{MgI_2} \longrightarrow 2\,\mathrm{RCOOMgI} + \mathrm{H_2} \qquad (1)$$

In the course of the reaction the iodomagnesium salt[5] suffers a partial decomposition into the magnesium salt and magnesium iodide, an equilibrium apparently being established between the components of the system

$$2\mathrm{RCOOMgI} \rightleftharpoons (\mathrm{RCOO})_2\mathrm{Mg} + \mathrm{MgI_2} \qquad (2)$$

Since magnesium iodide is thus being regenerated, it follows that a small amount of halide may suffice for a large amount of acid.

With the evolution of hydrogen from the acid at an end, reduction of the salt ensues. Since the hydrogen escapes as such, it is obvious that the reduction is not occasioned by the hydrogen but by the binary system. The reduction proceeds, presumably, along the following course



$$\begin{array}{c}\mathrm{OMgI}\\|\\\mathrm{RC{=}O}\\\mathrm{RC{=}O}\\|\\\mathrm{OMgI}\end{array} \xrightarrow[\mathrm{MgI_2}]{\mathrm{Mg}} \underset{(\mathrm{I})}{\begin{array}{c}\mathrm{OMgI}\\|\\\mathrm{RC{-}OMgI}\\|\\\mathrm{RC{-}OMgI}\\|\\\mathrm{OMgI}\end{array}} \longrightarrow \begin{array}{c}\mathrm{O}\\\|\\\mathrm{RC}\\|\\\mathrm{RC}\\\|\\\mathrm{O}\end{array} \xrightarrow[\mathrm{MgI_2}]{\mathrm{Mg}} \underset{(\mathrm{II})}{\begin{array}{c}\mathrm{OMgI}\\|\\\mathrm{RC}\\\|\\\mathrm{RC}\\|\\\mathrm{OMgI}\end{array}} \xrightarrow{\mathrm{HOH}} \begin{array}{c}\mathrm{OH}\\|\\\mathrm{RC}\\\|\\\mathrm{RC}\\|\\\mathrm{OH}\end{array} \longrightarrow \underset{(\mathrm{III})}{\begin{array}{c}\mathrm{RC{=}O}\\|\\\mathrm{RCH}\\|\\\mathrm{OH}\end{array}} \qquad (3)$$

Addition of water to the reduction mixture hydrolyzes the iodomagnesium compound of the stilbene-diol (II), and the corresponding benzoin (III) is produced. The yields of benzoins obtained varied, however, with the conditions of experiment and with the nature of the individual acid, and ranged from 30 to 75%. We have reason to assume that the glycolate (II) is practically the sole product of the reduction, and that the low yields of benzoin are due to some subsequent decomposition of the glycolate. Occasionally more than just a small amount of the corresponding benzil is produced, an indication that in such cases some of the product (I) has escaped further reduction to product (II).

Reaction of Esters.—Alkyl esters of aromatic acids are saponified by magnesium iodide in ether solution[6]

$$\mathrm{RCOOCH_2R'} + \mathrm{MgI_2} \rightleftharpoons \mathrm{RCOOMgI} + \mathrm{ICH_2R'} \qquad (4)$$

We found that this reaction proceeds in a solution refluxed on the steam-bath. Consequently, in the reaction of the ester with our binary system, saponification takes place first, and this is followed by reduction of the resulting iodomagnesium salt to the precursor (II) of benzoin. At the

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[5] Whether the iodomagnesium salt has the constitution assigned to it or whether it be of the type $(\mathrm{RCOO})_2\mathrm{MgMgI_2}$ [Ivanov, *Compt. rend.*, **185**, 505 (1927)], does not affect our discussion. However, like Grignard and others [Grignard, *Compt. rend.*, **185**, 507 (1927); Meisenheimer, *Ber.*, **61**, 708 (1928); Meisenheimer and Schlichenmaier, *Ber.*, **61**, 720 (1928)], we are of the opinion that the monomolecular formula best represents the structure of the salt.

[6] Zal'kind, *J. Russ. Phys.-Chem. Soc.*, **46**, 692 (1914).

same time the alkyl halide, which has resulted from saponification, reacts with the magnesium and there may thus be formed a hydrocarbon, $R'CH_2CH_2R'$, and also the Grignard reagent, $R'CH_2MgI$; the latter may in its turn react with unsaponified ester and with the salt. It may be mentioned that benzoin has been observed also as one of the products of the action of sodium on esters.

Aryl esters, as phenyl benzoate, are split in a manner different from that in the case of alkyl esters

$$RCOOAr + MgI_2 \rightleftharpoons RCOI + IMgOAr \ (Ar = Aryl) \qquad (5)$$

Since no iodomagnesium salt has been formed, no benzoin results on subsequent treatment with the binary system. The acyl iodide, we find, does not yield the stilbene glycolate on reduction, nor does it give rise to benzil when treated with metallic magnesium.[7]

Reaction of Peroxides.—Acyl peroxides react vigorously with magnesium iodide alone

$$RCOO{-}OOCR + 2MgI_2 = 2RCOOMgI + I_2 \qquad (6)$$

Likewise, bromine is set free from magnesium bromide. In the presence of magnesium, the halogen is converted into magnesium halide and the organic salt is then reduced to the stilbene-diol compound.

Experimental

Displacement of Hydrogen from the Acids.—Metallic magnesium reacts very slowly with the organic acids dissolved in anhydrous ether or benzene, or in a mixture of both, in the concentrations employed in our experiments (about 5%). Even on prolonged boiling with solutions of acids of twice that concentration only a small quantity of hydrogen is evolved. If, however, to the mixture a small amount of iodine or of magnesium iodide (3 to 10%) is added, the reaction sets in at once—vigorously at the start but soon subsiding. The metal before long becomes coated with the insoluble magnesium salt and the reaction stops entirely. On the other hand, if magnesium iodide is present in amount sufficient to furnish the halomagnesium salt (Equation 1), then the reaction goes to completion in a short time. After many preliminary experiments the following method was adopted as the most suitable for determining the quantity of hydrogen evolved.

A solution of 0.01 mole of magnesium iodide was prepared in 60 cc. of a mixture of ether and benzene (1:2) and a weighed amount of magnesium powder (usually 0.6 g.) was added. The reaction flask was attached by means of a ground-glass connection to a small condenser, from the top of which a capillary tube led to a gas buret filled with water. Between the condenser and buret was a calcium chloride tube. The acid (0.02 mole), in the form of pellets, was supported on a glass basket,[8] which was set above the level of the liquid and so arranged that when the solution was boiling the condensate dripped down upon the acid and brought it down into the solution only gradually. A steady stream of hydrogen was evolved into the buret and the reaction was at an end in fifteen to twenty minutes. In the following table are given representative values obtained with several acids.

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[7] Compare Staudinger and Anthes, *Ber.*, **46**, 1417 (1913); Tistchenko, *Bull. soc. chim.*, [4] **37**, 623 (1925); Karrer and co-workers, *Helv. Chim. Acta*, **11**, 233 (1928).

[8] Gomberg, This Journal, **45**, 401 (1923).

Table I

Hydrogen Displaced in Reaction $RCOOH + Mg + MgI_2$

Acid	Mg diss., % of calcd.	H % of calcd.	Acid	Mg diss., % of calcd.	H % of calcd.
Benzoic	108	89	Phenylacetic[a]	103	117
p-Toluic	102	81	Diphenylacetic	94	97
α-Naphthoic	100	86	Stearic	90	87
β-Naphthoic	104	93			

[a] We have repeated this experiment several times, using most carefully purified acid, and have always obtained the high yield of hydrogen. We wonder whether this may not be due to replaceability of the hydrogen in the alkyl group, similar to what Kohler, Stone and Fuson, This Journal, **49**, 3181 (1927), have found to be the case with many compounds toward the Grignard reagent.

The formation of hydrogen in our reaction depends primarily upon liberation of hydrogen iodide, which then reacts with the metallic magnesium $RCOOH + MgI_2 \rightleftharpoons RCOOMgI + HI$; $Mg + 2HI \longrightarrow MgI_2 + H_2$. The presence of the equilibrium was demonstrated by the following experiment. A mixture of benzoic acid and magnesium iodide, without metallic magnesium present, was refluxed for twenty-four hours; under these conditions the HI, which otherwise would have reacted with magnesium, was now continually being removed through its reaction with the ethyl ether, tending to form ethyl iodide.[9] From 12.2 g. of acid and 32 g. of MgI_2, 12.3 g. of ethyl iodide was obtained. Even in the presence of metallic magnesium this reaction took place to some extent. This reaction, and loss of some HI carried away by escaping hydrogen, accounts for the low yields of hydrogen obtained (Table I).

That hydrogen iodide, under the conditions of our experiments, does react with magnesium in the presence of ether with evolution of hydrogen was definitely established.[10] Dry hydrogen iodide was passed into benzene and it was found that this solution did not react with magnesium. However, addition of an equal volume of ether to this mixture induced *immediate* reaction with extremely lively evolution of hydrogen. The quantity of gas corresponded to 96% of the magnesium that had been dissolved. We found also that hydrogen bromide and magnesium react in a mixture of ether and benzene with evolution of hydrogen. Though HCl alone in ether-benzene did not react, the addition of $MgBr_2$ brought about a reaction. On several occasions we analyzed the seemingly homogeneous crystalline deposit that had separated and found it to be not far from the composition BrMgCl, or $MgCl_2 \cdot MgBr_2$.

If the reaction mixtures from the organic acids are hydrolyzed soon after all of the hydrogen has been evolved, practically all of the acid can be recovered unchanged from the aqueous solution of its salts. In the case of benzoic acid traces of hexahydrobenzoic acid were unmistakably recognized. Prior to hydrolysis the iodomagnesium salts separated from the solution usually as insoluble, oily etherate compounds; in rare cases crystallization set in. We isolated and analyzed these solid products and found that they consist of mixtures of the halomagnesium and the normal magnesium salts of the acids. In one instance, with benzoic acid, the crystalline compound was almost entirely the pure salt RCOOMgI.

Magnesium bromide was found to give insoluble addition products with organic acids, $2RCOOH \cdot MgBr_2 \cdot 2C_4H_{10}O$. As a rule the corresponding magnesium iodide

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[9] Silva, *Ber.*, **8**, 904 (1875); Cottrell and Rogers, *Am. Chem. J.*, **21**, 64 (1899).

[10] Zelinsky, *J. Russ. Phys.-Chem. Soc.*, **35**, 404 (1903); see, however, Hess and Rheinboldt, *Ber.*, **54**, 2043 (1921).

compounds were soluble under similar conditions. With toluic acid, however, a crystalline compound of the composition $2RCOOH \cdot MgI_2 \cdot 2C_4H_{10}O$ was formed.

Reduction of Acids

The amount of magnesium iodide employed for reduction usually corresponded to that required by the formulation (3). Frequently much less was used in virtue of the ability of the iodomagnesium glycolate to lose MgI_2.[11]

Reduction of Benzoic Acid.—A mixture of magnesium + magnesium iodide was prepared from 95 g. (0.75 atom) of iodine and 20 g. of magnesium powder in 100 cc. of ether and 200 cc. of benzene. To this colorless mixture 30.5 g. (0.25 mole) of benzoic acid was added in portions. When the lively evolution of gas had ceased, the mixture, protected from air by means of a mercury trap, was heated on the steam-bath. After five days of heating the dark, reddish-brown solution was filtered from the undissolved magnesium and treated with water. Dilute acid was added to dissolve the copious precipitate of magnesium hydroxide that had been produced. The organic solution was extracted with dilute sodium carbonate solution, which removed unchanged benzoic acid. Evaporation of the solvents left a solid contaminated with some oily by-products, and these were removed by digestion of the crude product with ether. The residue consisted of practically pure benzoin, and weighed 12.0 g., which represents a yield of 30%. From the ether extract a small amount of benzoin and benzil were isolated. In another experiment the yield of benzoin was 43%. One reason for the reaction being incomplete appears to be the precipitation of an insoluble material upon the magnesium, probably an etherate of $(MgI)_2O$. The reaction was also carried out at room temperature. A mixture prepared exactly as above, after having been shaken for eighteen days, yielded on hydrolysis 34% of benzoin and 4% of benzil. The remainder was mostly unchanged benzoic acid, with hardly any oily by-products such as occur when the reaction has been carried out by the aid of heat.

Prior to hydrolysis the reduction product is the iodomagnesium salt of stilbene-diol. Its reactions were compared with those of the same glycolate but made directly from benzil, and were found to be identical: treated with iodine, it gave benzil: with benzoyl chloride, the stilbene-diol dibenzoate, m. p. 156°, was formed.

For further verification of our inference that benzoin comes from the reduction of the salt $C_6H_5COOMgI$, we have prepared that salt by two standard methods: $RCOOH + CH_3MgI \longrightarrow RCOOMgI \longleftarrow CO_2 + IMgR$. In each case the reaction mixture was heated with metallic magnesium and the final results were 46% and 20% yields of benzoin, respectively. In some instances one may find it desirable, from the preparative point of view, to make a benzoin from the aryl halide without isolation of the intermediately formed acid. We have done so with benzoin and α-naphthoin from phenyl bromide and naphthyl bromide, respectively.

Reduction of *p*-Toluic Acid.—Taken for experiment: 13.6 g. (0.1 mole) of *p*-toluic acid, 38 g. (0.3 atom) of iodine and 10 g. of magnesium powder in 150 cc. of benzene-ether (2:1). In a short time the evolution of gas was at an end and the mixture was gently refluxed on the steam-bath for three days. The dark, reddish-brown solution was filtered and decomposed with water. A large amount of toluic acid was extracted from the solution by sodium carbonate. The reduction product was found to consist for the most part of dimethyl benzil rather than the benzoin. Consequently the entire crude product was oxidized to the benzil by heating it for several hours with 8 g. of copper sulfate, 8 g. of pyridine and 4 g. of water. After purification the *p,p'*-dimethyl benzil

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[11] Gomberg and Bachmann, THIS JOURNAL, 49, 2589 (1927).

weighed 3.59 g. (30% yield). The substance melted at 102–104°, and it was found to be identical in all respects with the dimethyl benzil obtained from *p*-tolualdehyde through the benzoin condensation.

Reduction of α-Naphthoic Acid.—To the binary system prepared from 15 g. (0.1 atom) of iodine and 10 g. of magnesium powder in 120 cc. of 1:1 ether–benzene, 17.2 g. (0.1 mole) of α-naphthoic acid was added in portions of several grams at a time. After hydrogen had ceased coming off, the mixture was heated. In a few minutes the solution became green in color, then greenish-brown and finally dark reddish-brown. After seven hours the heating was discontinued and the mixture was hydrolyzed. The naphthoic acid that was recovered by extraction with sodium carbonate was contaminated with a gummy product which was found to be very soluble in cold benzene and could thus be removed, leaving 3.05 g. of naphthoic acid. Evaporation of the ether–benzene solution left a residue consisting of a mixture of naphthoin, naphthil and some oil. For a determination of the extent of reduction which the acid had suffered, the crude product was oxidized by means of copper sulfate and pyridine to naphthil. The oxidation product was recrystallized from benzene and obtained in the form of pale yellow needles; m. p. 189–190°; weight, 4.85 g., which is equal to 31% of that possible. Our α-naphthil was found to be identical with the product obtained by oxidation of α-naphthoin which had been prepared from the naphthaldehyde. Although the conditions of reduction of the acid were varied over a wide range, the yield of α-naphthoin or naphthil invariably ran between 30 and 35%.

Reduction of β-Naphthoic Acid.—Taken for reaction: 17 g. of iodine, 12 g. of magnesium, 200 cc. of ether–benzene, 17.2 g. of β-naphthoic acid. A few minutes after evolution of hydrogen had ceased, the mixture became light green, then dark green and finally dark reddish-brown in color. After eleven hours the solution was filtered and decomposed with water. The amount of unchanged naphthoic acid was 8% and the reduced product consisted of naphthoin mixed with a considerable quantity of naphthil. The mixture was oxidized by means of copper sulfate and there was thus obtained 11 g. of pure recrystallized β-naphthil, which represents a yield of 70%. Several smaller runs gave yields as high as 75%. From hot benzene the β-naphthil crystallizes in cream-colored needles; m. p. 157–158°.

Anal. Calcd. for $C_{22}H_{14}O_2$: C, 85.18; H, 4.55%. Found: C, 84.90; H, 4.84. *Mol. wt.* Calcd.: 310. Found: 323.

The amount of metallic magnesium dissolved in the course of the reduction process and the magnesium hydroxide produced on hydrolysis of the reduction mixture were determined and they were found to correspond to that required by formulation (3).

Reduction of *p*-Phenylbenzoic Acid.—A mixture of 4.0 g. of *p*-phenylbenzoic acid, 4.0 g. of magnesium iodide and 5 g. of magnesium powder in 60 cc. of benzene–ether (2:1) was heated for five days. In the course of the reaction the solution became green and then reddish-brown in color. After hydrolysis a small amount of unchanged acid was recovered and from the reduction product, after treatment with copper sulfate, 1.7 g. (46%) of *p,p'*-diphenyl benzil was obtained. It was recrystallized from a mixture of alcohol and benzene and was obtained in the form of yellow needles, m. p. 139–140°. It was identical with *p,p'*-diphenyl benzil which had been synthesized through the benzoin condensation from *p*-phenylbenzaldehyde.

Reaction of Esters with Mg + MgI_2

Saponification of Benzyl Benzoate by Magnesium Iodide.—Fifty-three grams (0.5 mole) of benzyl benzoate was added to a solution of 70 g. of magnesium iodide in 300 cc. of ether–benzene (1:2), and the resulting solution was heated on the steam-bath for one week. The red solution was then poured into water. In the aqueous solution was found 30.32 g. (99%) of benzoic acid in the form of water-soluble salts. The ether–benzene solution was dried over anhydrous sodium sulfate and then concentrated to a small volume. On being cooled the solution deposited a large amount of benzyl iodide. By recrystallization from alcohol, 20 g. of pure benzyl iodide was obtained.

Reduction of Benzyl Benzoate.—Taken for experiment: 25.6 g. (0.2 atom) of iodine, 10 g. of magnesium and 21.2 g. (0.1 mole) of the ester, in 120 cc. of the mixed solvents. After a day the greenish color initially formed changed to brown and later to reddish-brown. After being heated for a week the solution was filtered and hydrolyzed. From the ether–benzene solution was obtained a mixture of bibenzyl and benzoin, and they were separated from each other by dissolving the former in petroleum ether. After purification the bibenzyl weighed 6.2 g. (70%) and the benzoin amounted to 4.8 g. (45%).

Methyl Benzoate.—Thirty-four grams of this ester was heated with the proper amount of magnesium + magnesium iodide, and yielded 2.2 g. of benzoin. Here the yield of benzoin is necessarily small because the methyl iodide that is produced on saponification forms readily with the magnesium a Grignard reagent, which in turn is able to react with the ester or salt.

Phenyl Benzoate.—No benzoin was obtained on heating 10 g. of phenyl benzoate with the reducing mixture. The main products were phenol, 4.2 g. (90%) and a resinous mass which was found to be soluble in the usual organic solvents, but no crystalline products were obtained for identification. We find that benzoyl iodide treated with the binary system gives resins of a similar nature.

Reaction between Benzoyl Peroxide and Mg + MgI_2.—A solution of 4.88 g. (0.2 mole) of benzoyl peroxide in 50 cc. of benzene was slowly added to a solution of magnesium iodide in ether–benzene. The very first drop of the peroxide solution liberated iodine, and as more solution was added the mixture became dark red and a heavy oil of the etherate of iodomagnesium benzoate separated. After twenty hours the mixture was poured into water. From the aqueous solution, on acidification, 4.90 g. (100%) of benzoic acid was obtained. Titration by standard thiosulfate solution showed the presence of 5.0 g. (99%) of iodine. In the same manner benzoyl peroxide liberated bromine from magnesium bromide.

For reduction, 30.3 g. of benzoyl peroxide was cautiously added to a mixture of magnesium and magnesium iodide prepared from 65 g. of iodine and 10 g. of magnesium in 300 cc. of ether–benzene. Each addition of peroxide was accompanied by hissing and crackling noises, and by liberation of iodine. Most of this iodine reacted at once with the magnesium. The grayish mixture was heated for four days. Hydrolysis then gave 12 g. of benzoin, which represents a yield of 45%.

Summary

Organic acids in solution in ether and benzene react vigorously with the binary system Mg + MgI_2, hydrogen is evolved and the acid is converted completely into the salt RCOOMgI. This salt then undergoes reduction and, at least in the case of aromatic acids, the reduction product is R(IMgO)C=C(OMgI)R, which when hydrolyzed gives rise to the corresponding benzoin in yields of 30 to 75%. The reducing effect of the binary system is ascribed to the intermediate formation of the compound MgI.

Alkyl esters of aromatic esters and acyl peroxides are reduced by the binary system in a similar manner. Aryl esters are affected differently.

The reduction of acids or of esters by this binary system offers a con-

venient method for obtaining benzoins. This method should prove particularly useful in those instances when the aldehyde requisite for the usual benzoin condensation is not readily accessible.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 33]

THE RELATIVE RATES OF BROMINATION OF THE OLEFINS[1]

BY HAROLD S. DAVIS[2]

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This paper deals mainly with experimental work on the rates of reaction of the lower olefins with bromine, particularly in carbon tetrachloride solution.

1. The Dark Reaction of Ethylene with Bromine in Dry Carbon Tetrachloride Solution Is Very Slow.—Contrary to general belief,[3] it was found that ethylene brominates in carbon tetrachloride at a rate measurable with time and that if the solutions are dried and kept away from bright light, the reaction requires hours and even days for completion.

2. The Rate of the Dark Reaction of Ethylene with Bromine in Carbon Tetrachloride Varies Greatly with the Quantity of Moisture in the Solution.—Solutions of bromine in carbon tetrachloride were dried in the following ways: (*a*) by refluxing for four hours with phosphorus pentoxide and distilling into a dry receiver protected from moisture in the air by phosphorus pentoxide. In some cases the solution was first shaken for several days with phosphorus pentoxide before refluxing and distilling. (*b*) By shaking for different periods of time with phosphorus pentoxide and settling. Evaporation tests on the clear supernatant liquid showed that it contained less than one part of phosphorus pentoxide in one hundred thousand by weight.

When dry ethylene was added to these solutions the reaction went quite

[1] This paper contains results obtained in an investigation on the "Relative Rates of Reaction of the Olefins," listed as Project No. 19 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by Mr. John D. Rockefeller. This fund is being administered by the Institute with the coöperation of The Central Petroleum Committee of the National Research Council.

[2] Director and Research Associate, Project No. 19.

[3] Thus Plotnikov, "Lehrbuch der Photochemie," **1920**, pp. 245–255, states that ethylene and bromine unite to form the dibromide at ordinary temperatures instantaneously and completely and the reaction only slackens to one measurable with time at −100°. Working at this temperature in petroleum ether solution, he found the reaction to be of the second order. On the other hand, Stewart and Edlund, THIS JOURNAL, **45**, 1014 (1923), found ethylene and bromine to be practically unreactive in the gaseous state.